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MODELING OF NON-IDEAL ALUMINIZED EXPLOSIVES

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Abstract

We have implemented a Wood-Kirkwood kinetic detonation model based on multi-species equations of state and multiple reaction rate laws. Finite rate laws are used for the slowest chemical reactions, while other reactions are given infinite rates and are kept in constant thermodynamic equilibrium. Within the context of WK theory, we study the chemical interaction between Al and HMX detonation products in non-ideal explosives. We develop a kinetic rate law for the combustion of Al in a condensed detonation that depends on the pressure and the detonation product gases. We use a Murnaghan form for the equation of state of the solid and liquid Al and Al_2O_3 . We find that we can replicate experimental detonation velocities for HMX/Al composites to within a few percent for a wide range of aluminum content. We discuss the uncertainties in our model and the implications of our results on the modeling of other non-ideal explosives

INTRODUCTION

The detonation of an energetic material is the result of a complicated interplay between chemistry and hydrodynamics. While the detailed chemical kinetics of detonation in gases have been extensively studied, much less is known regarding chemical kinetic processes governing condensed energetic materials. The primary reason for this is the extreme pressure and temperature immediately behind the detonation wave: pressures of 400 kBar (40 GPa) and temperatures of 4000K are common. The extreme conditions result in very broad spectroscopic features that make the identification of individual chemical species very difficult.

There is a continuing need in the energetic materials field for reliable predictions of detonation velocity and energy delivery. This has traditionally been accomplished through the means of Chapman-Jouget thermodynamic detonation theory. Chapman-Jouget detonation theory assumes that thermodynamic equilibrium of the detonation products is reached instantaneously. For the case of "non-ideal" explosives, especially ones containing Al, this may not be the case.

In this study we consider the behavior of "non-ideal" aluminized explosives. In particular, we consider HMX/Al composites, for which there is

recent experimental data.¹ We define non-ideal explosives as those with a reaction zone of one mm or more. They are often poorly modeled by Chapman-Jouget theory. These materials have chemical reaction rates that are slow compared to hydrodynamic time scale 10^{-6} s so that the Chapman-Jouget (CJ) assumption of instantaneous thermodynamic equilibrium breaks down. For example, it is found experimentally that the detonation velocity of non-ideal explosives varies sharply from the CJ value and depends strongly on the charge radius. We therefore consider the interaction of chemical kinetics with the detonation wave in order to reach an acceptable representation of detonation in non-ideal explosives. Wood and Kirkwood² (WK) proposed a two dimensional steady state kinetic detonation theory that includes time-dependent kinetics and steady-state detonation wave propagation. WK considered a cylindrical charge of infinite length. They solved the hydrodynamic Euler equations in the steady state limit along the central streamline of the cylinder. Radial expansion was treated as a source term in the 1-D flow along the streamline.

In such a case, it is found that the detonation velocity depends on the interplay between chemical kinetics and radial expansion. In the limit of no radial expansion, the ZND plane wave result is obtained. When radial expansion is allowed

however, the detonation velocity can vary from the C-J prediction. In the limit of strong radial expansion the detonation wave fails; no velocity is found which satisfies the steady-state equations.

In the present paper we implement a model of detonation kinetics based on the identification of individual chemical species. The advantage of the present treatment is that the same equations of state and chemical rate laws can be used on a wide range of explosive mixtures. A mixture equation of state based on thermal, mechanical, and partial chemical equilibrium is used. The mixture model is implemented in the Cheetah thermochemical code³. Small molecules that are gases at standard conditions are treated with the BKW⁴ real gas equation of state. Solids are treated with a modified form of the Murnaghan⁵ equation of state. Simple pressure-dependent chemical reaction rates are employed. These rates represent the consumption of the energetic material by the detonation wave. Fast reaction rates (partial chemical equilibrium) are assumed for species other than the initial material.

The Wood-Kirkwood equations are solved numerically to find the steady-state detonation velocity. From a previous study, we have determined pressure-dependent kinetic reaction rates for a wide range of explosives and binders, including HMX⁶. The radial expansion was derived from measured radii of curvature for the materials studied. We find good agreement with measured detonation velocities using the same set of equations of state and rate laws for each composite. Although our treatment of detonation is by no means exact, the ability to model a wide range of phenomena based on simple equations of state and rate laws is encouraging. We find that the inclusion of detonation kinetics yields a significant improvement in the predicted detonation velocity of materials with long estimated reaction zones. More importantly, we are able to reproduce the dependence of the detonation velocity on charge radius for several materials. For materials with short reaction zones, we recover the results of Chapman-Jouguet thermochemistry.

WOOD-KIRKWOOD DETONATION THEORY

WK theory starts with the hydrodynamic Euler equations coupled to chemical kinetics. The theory treats the detonation along the center of the cylinder. The Euler equations are reduced to their steady state form. The result is a set of ordinary differential equations that describe hydrodynamic variables and chemical concentrations along the center of the cylinder.

The notation is as follows: we use cylindrical coordinates in a frame moving with the shock velocity D . x is the axial coordinate, r is the radial coordinate and u is the axial particle velocity in the moving frame (equal to $D-U$ in the lab frame). The radial velocity is called ω . Subscripts denote a spatial derivative.

$$\begin{aligned} u_x &= \psi / \eta \\ \rho_x &= -(\rho/u)(u_x + 2\omega_r) \\ E_x + p v_x &= 0 \\ F_x &= \mathbf{R} / u \\ \omega_r &= (D - u(t=0)) / R_c \end{aligned} \quad (1)$$

where F is the concentration vector, \mathbf{R} is the reaction rate vector and R_c is the radius of curvature. ρ is the density, p is the pressure, E is the specific energy and v is the specific volume. We take the form of these equations from Fickett and Davis⁷ (see Equations 5.28 and 5.37). The expression for ω_r is an approximation that is strictly valid only at the initial jump off of the shock. The reaction rate vector \mathbf{R} is defined, such that

$$d\lambda_i / dt = \mathbf{R}_i \cdot (1 - \lambda_i) \quad (2),$$

where λ represents the amount of unburned reactant normalized to vary between 0 (all unburned) and 1 (all burned).

We define

$$\eta \equiv 1 - u^2/c^2 \quad (3)$$

to be the sonic parameter, where c is the speed of sound. If the sonic parameter η is greater than zero communication with the shock front is possible. If it is less than zero the region cannot communicate with the shock front. Secondly, we will define the pressure production term

$$\psi \equiv (\partial P / \partial F)_{v,E} \mathbf{R} / \rho c^2 - 2\omega_r \quad (4)$$

Chemical reactions that increase the pressure at constant v,E will increase the value of ψ . Radial expansion, however, decreases the pressure through the ω_r term.

APPLICATION TO ALUMINIZED EXPLOSIVES

We perform calculations for various mixtures of HMX and Al particles and compare our results with the recent experimental results of Gogulya et al.¹. In addition to varying the Al content, they also varied the Al particle size from 0.5 μm to 150 μm . We

modeled these experiments with the HMX kinetic rate law from the previous study⁶ and determined an Al combustion rate that best fit the experimental data. We use a rate that depends on pressure, the concentration of H₂O and a surface term. The rate proportional to $[1-\lambda]^{2/3}$ means that the rate is surface area limited, while the rate being proportional to $n(\text{H}_2\text{O})$ gives the rate an initiation delay. We find the rate for Al combustion that gives the best fit to the data is of the form:

$$R = 0.0002 \cdot n(\text{H}_2\text{O}) \cdot [1-\lambda]^{2/3} \cdot P^2 \mu\text{s}^{-1} \quad (5)$$

where $n(\text{H}_2\text{O})$ is the concentration of H₂O in units of moles/kg of explosive and P is in units of GPa. For the rate of HMX decomposition we use

$$R = 0.3P^2 \mu\text{s}^{-1} \quad (6)$$

where P is in units of GPa.

For this study, we have used a BKW equation of state for product gases with parameters fit only to ideal explosives⁶. For Al and Al₂O₃ we have implemented a modified Murnaghan form that fits both shock hugoniot data and the melting curve for both Al and Al₂O₃. We find that the untreated Al is in the liquid state during the detonation.

The results of our calculations are shown in Figure 1. However, we cannot replicate the Al particle-size dependence of the detonation velocity. A simple surface area scaling of the rate does not replicate the experimental particle-size dependence. For the case of an Al particle size of 0.5 μm , excessive Al₂O₃ coating of the particles may quench the Al combustion. Our rate law simulates the general trend of decreasing detonation velocity with increasing the amount of Al in the composite for larger particle sizes. This rate law predicts that only a relatively small fraction of the Al reacts in the detonation wave.

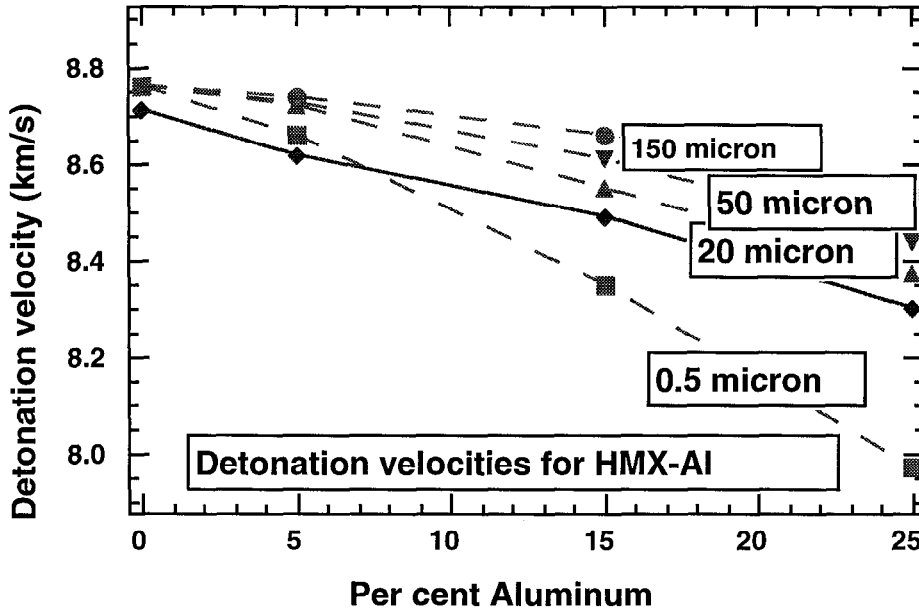


FIGURE 1. Detonation velocities for HMX/AL Composites as a function of Al concentration and particle size. Experimental values (connected by dashed lines) from Ref. 1 are compared to a Kinetic Cheetah calculation (connected by solid line).

Figures 2 and 3 show calculated time histories of the temperature and pressure for various composites. Gogulya et al. measured the temperature and pressure profiles in their experiments with the aid of a dual-channel optical pyrometer. The brightness temperature estimated by measuring the time dependent luminosity intensity at the surface of the composite. The pressure profile was estimated by measuring the temperature response of a liquid boroform layer and using an estimated estimated pressure-temperature response function. Our

calculated temperature and pressure profiles are very similar to those estimated by Gogulya et al. for a Al particle size of 50 μm . That is, the calculated temperatures and pressures are in the range of the experimental values and have the measured dependence on Al content.

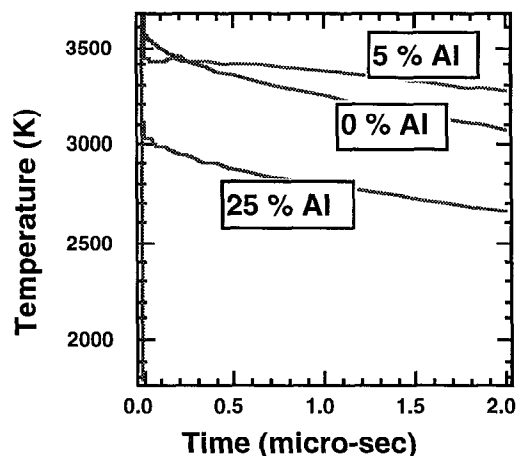


Figure 2. Calculated temperature as a function of time for various HMX-Al composites.

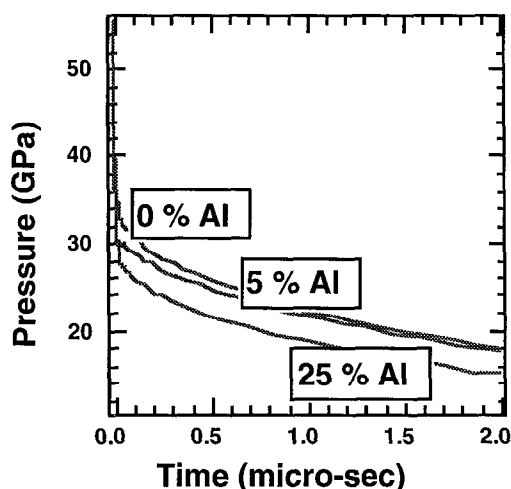


Figure 3. Calculated pressure as a function of time for various HMX-Al composites.

In conclusion we have developed a kinetic model for thermochemical detonations based on Wood-Kirkwood theory and the thermochemical Cheetah code. We have applied this model to the case of non-ideal explosives with significant Al content. We find that with a simple model for kinetic processes we are able to model many of the features of non-ideal explosives such as their detonation velocities and the time-dependence of the temperature and pressure. In the future, we plan to extend our kinetic modeling study to include both temperature and pressure dependent rate laws. In this way we can extend our model to more physically based rate laws and study more complex non-ideal detonation behavior such as shock initiation, hot spot formation and failure processes.

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